U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-297 753

Chemical Technology and Economics in Environmental Perspective. Task IV - Potential Worker and Consumer Exposure to Nitrilotriacetic Acid (NTA) in Detergents

Midwest Research Inst., Kansas City, MO

Prepared for

Environmental Protection Agency, Washington, DC

Jun 79

PB 297753

United States
Environmental Protection
Agency

Office of
Toxic Substances
Washington DC 20460

EPA-560/11-79-008
June 1979

Toxic Substances

EPA

Potential Worker and Consumer Exposures to Nitrilotriacetic Acid (NTA) in Detergents

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA 560/11-79-008		PB297753

4. TITLE AND SUBTITLE	5. REPORT DATE
Potential Worker and Consumer Exposures to Nitrilotriacetic Acid (NTA) in Detergents	June 1979
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Alfred F. Meiners, Thomas W. Lapp, Charles E. Mumma, Eugene G. Podrebarac, Robert P. Reisdorf, Harold P. Owens, and Howard Gadberry	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Midwest Research Institute 425 Volker Boulevard Kansas City, Missouri 64110	Task IV
	11. CONTRACT/GRANT NO. 68-01-3896

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Protection Agency Office of Toxic Substances Washington, D.C. 20460	Final Report
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

Roman Kuchkuda, Project Officer

16. ABSTRACT

The current annual production of trisodium nitrilotriacetate in the United States is approximately 70 million pounds. The production of NTA is highly automated and is largely under remote controls; thus, production workers have little potential for exposure. Analysis of air in the workers' breathing zone indicated that the highest exposure area had an average potential exposure of 8.2 mg NTA/day. NTA was not detected in urine samples of production workers (detection limit, 0.5 mg/liter). The number of detergent production workers that would be directly exposed to airborne detergent dust is estimated to be 2,500; typical exposure during detergent formulation is estimated to be 338 μg/NTA/day. Consumer exposure to detergents can result from inhalation of detergent dust, percutaneous absorption from contact with wash water or direct skin contact with the detergent, ingestion of residue on dishes or utensils, and skin contact with residues in clothing. Estimates of the number of consumers potentially exposed (and the extent of exposure) are as follows: automatic clothes washing, 176 million (0.05 to 0.35 μg NTA/day); automatic dishwashing, 33 million (0.009 to 0.14 μg NTA/day); hand dishwashing, 171 million (8.75 to 17.5 μg NTA/day); residue on dinnerware, 40 million (4.9 to 966 μg NTA/day); and general cleaning, 176 million (8.75 to 17.5 μg NTA/day).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Nitrilotriacetic acid NTA Production Exposure Detergent Consumer Worker		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Unlimited distribution	Unclassified	49
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	A03-A01

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-560/11-79-008

CHEMICAL TECHNOLOGY AND ECONOMICS IN ENVIRONMENTAL PERSPECTIVE

Task IV - Potential Worker and Consumer Exposure to Nitrilotriacetic Acid (NTA) in Detergents

FINAL REPORT
June 1979

Prepared under

Contract No. 68-01-3896

For

U.S. Environmental Protection Agency
Office of Toxic Substances
401 M Street, S.W.
Washington, D.C. 20460

Mr. Roman Kuchkuda
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PREFACE

This report presents the results of a study to assess and predict worker and consumer exposure to nitrilotriacetic acid in detergents.

This study was performed by Midwest Research Institute, as Task IV, under Contract No. 68-01-3896 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. The Office of Toxic Substances' project officer for this study was Mr. Roman Kuchkuda.

Midwest Research Institute would like to thank Ms. Justine Welch, Environmental Protection Agency, Office of Toxic Substances, for her valuable assistance during the course of this task. Her effort in providing Midwest Research Institute with industry contacts and data, as well as review comments, is sincerely appreciated. The cooperation of personnel from the Procter and Gamble Company, Monsanto Company, and W. R. Grace Company is sincerely appreciated.

Principal Midwest Research Institute contributors to this study included: Dr. Alfred F. Meiners (Task Leader), Principal Chemist; Mr. Charles Mumma, Senior Chemical Engineer; Dr. Eugene Podrebarac, Senior Chemist; Mr. Robert Reisdorf, Associate Occupational Health Scientist; Mr. Harold Owens, Associate Industrial Chemist; and Mr. Howard Gadberry, Senior Advisor for Technology. Mr. Albert E. Stewart, President, Stewart Industrial Hygiene Service, acted as consultant. Dr. Thomas W. Lapp is the project leader for this contract, under the supervision of Dr. Edward W. Lawless, Head, Technology Assessment Section.

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CONTENTS

Preface iii
Figures vi
Tables. vi

1. Introduction and Objectives. 1
2. Summary. 2
   Human exposure during manufacture 2
   Human exposure during detergent formulation 4
   Consumer exposure to detergents 5
3. Human Exposure During Manufacture. 7
   Production technology for trisodium nitrilotriacetate . . . 7
   Estimated number of U.S. production workers for NTA 12
   Analysis of probable worker exposure to NTA in manufacturing operations 13
   Worker exposure data. 14
   References to Section 3 19
4. Human Exposure During Detergent Formulation. 20
   Description of detergent formulation process. 20
   Areas in exposure in detergent plants 20
   Number of workers exposed 21
   Exposure levels 21
   References to Section 4 24
5. Consumer Exposure to Detergents. 25
   Number of consumers exposed 25
   Extent of exposure. 29
   References to Section 5 40

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FIGURES

Number		Page
1	General schematic for commercial production of trisodium nitrilotriacetate	9

TABLES

Number		Page
1	Summary of Potential NTA Exposure From Detergent Products . . .	3
2	Impurities in Trisodium Nitrilotriacetate	10
3	Potential Number of Consumers Exposed to NTA Via Detergent Usage	26
4	Potential Exposure to NTA From Consumer Use of Detergent Products.	30
5	Dust Levels From Powdered Detergents.	33
6	Inhalation Exposure to NTA-Containing Powdered Detergent. . . .	34

SECTION 1

INTRODUCTION AND OBJECTIVES

Nitrilotriacetic acid (NTA) is being considered as a partial replacement for phosphates in detergents produced in the United States. Currently, NTA is manufactured by Monsanto and W. R. Grace, who export the material to the Canadian detergent market and supply it for use in certain industrial processes. Current Canadian household detergent products are limited to 2.2% phosphorus. The NTA content of these detergents ranges from 0 to 25%; the industry-wide average of 15% is based on total poundage of detergent and the quantity of NTA sold in Canada.

The Environmental Protection Agency (EPA) is concerned about the possible consequences of NTA use in detergents in the United States. The purpose of this investigation is (a) to assess current workplace (worker) exposure to NTA during manufacture and formulation, and (b) to predict the possible future extent of worker and consumer exposure if NTA production and use in detergents were increased to 1 billion pounds per year. Exposure by way of drinking water was not a part of this effort, nor were health effects information; these topics are under consideration in EPA

SECTION 2

SUMMARY

A summary of the potential for exposure to NTA during manufacture, formulation, and consumer use is presented in Table 1.

HUMAN EXPOSURE DURING MANUFACTURE

The production of NTA is highly automated and is largely under remote controls. Thus, production workers have little potential for exposure to process chemicals except in the bagging and loading operations of the final product, the trisodium salt of NTA.

Production Technology

Trisodium nitrilotriacetate, the sodium salt of NTA, is currently being produced in the United States by Monsanto Chemical Company and by the W. R. Grace Company. The combined production from the Monsanto and W. R. Grace plants is currently approximately 70 million pounds of NTA per annum.

The W. R. Grace production process involves three steps: (a) the reaction of formaldehyde and ammonia to give hexamethylenetetramine (HMT), (b) the reaction of hydrogen cyanide (HCN) with HMT to give nitrilotriacetonitrile, and (c) the hydrolysis of nitrilotriacetonitrile by sodium hydroxide to give trisodium nitrilotriacetate. The Monsanto plant also uses this process under a licensing agreement.

Based on information provided by W. R. Grace and Monsanto, a total of only 32 workers are estimated to be involved currently in production of NTA in U.S. plants. For a projected NTA production rate of 400 million pounds per year, an estimated labor force of 57 workers would be required. A rate of 1 billion pounds per year would require 98 to 120 workers.

Analysis of Probable Worker Exposure

The entire NTA production process is automated and all regular shift workers, except those engaged in product packaging and loading activity, are normally located in a remote control room, separated from the process operations.

TABLE 1. SUMMARY OF POTENTIAL NTA EXPOSURE FROM DETERGENT PRODUCTS

Exposure source	Potential No. of persons exposed	Potential exposure (μg NTA/day)
NTA manufacture	98-120[a]	< 100-500[b] 8,200[c]
Detergent formulation	2,500[a]	< 338-3,380[d]
Consumer products[e]		
Powdered laundry detergent		
Automatic clothes washer	176×10^6	0.05-0.35
General cleaning	176×10^6	8.75-17.5
Residue on clothes	212×10^6	1.28
Hand dishwashing	5×10^6	8.75-17.5
Residue on dinerware	6×10^6	4.9-966
Powdered dishwashing detergent		
Automatic dishwashing	33×10^6	0.009-0.140
Residue on dinnerware	40×10^6	4.9-966
Light-duty detergent		
Hand dishwashing	171×10^6	8.75-17.5
Residue on dinnerware	206×10^6	4.9-966
General cleaning	176×10^6	8.75-17.5

a/ Assumes NTA annual production of 1 billion pounds.

b/ Normal line workers - no respirators.

c/ Hopper car loaders - no respirators.

d/ The exposure values are "typical" and "extreme," respectively.

e/ Adult levels.

Air monitors located at various points in the plant area trigger an alarm in the event of any process leaks of toxic material (e.g., HCN).

Dust losses of product are apt to occur to the work atmosphere of the drying kiln, the product packaging area, and the product bulk loading operations. Therefore, the risk of worker exposure via both skin contact and inhalation appears to be greatest for these operations.

Worker Exposure Data

Actual worker exposure data have been compiled at the Monsanto facility. This study included representation of all job classifications in the plant. Urine samples were taken for analysis and the air in the breathing zone of each worker was monitored. NTA was not detected in the urine samples (detection limit, 0.5 mg/liter by gas chromatography/mass spectrometry (GC/MS)).

The highest exposure area, the hopper car loader area, had an average potential exposure of 8.2 mg NTA per 8-hr workday. In this area the workers normally wear protective clothing and equipment during periods of high exposure risk.

HUMAN EXPOSURE DURING DETERGENT FORMULATION

The Detergent Formulation Process

The use of NTA as a replacement for sodium tripolyphosphate in detergents would not require changes in the current formulating process in the United States.

The method currently being used for the commercial formulation of granular detergents is primarily a batch process, in which raw ingredients are pumped or conveyed through a closed system to reactors and mixers, and then blended into a slurry. The slurry is sprayed from the mixer into drying towers to achieve the desired granulation size and moisture content. The finished powder is then conveyed to production lines where it is automatically put into cartons and packed for shipping.

Liquid laundry detergents and powdered cleansers are also formulated primarily by batch processes in a closed system.

Areas of Exposure in Detergent Plants

The workplace atmosphere can become contaminated with detergent dust containing NTA from abnormal events such as leaks in the product lines and spills caused by a malfunction in equipment; routine and nonroutine equipment cleanup operations can also contribute to worker exposure. Operations which require manual handling of bags of NTA and the filling and packing production lines

can become high dust areas, particularly when powder is spilled as a result of machine jams and product changeovers. In these situations, worker exposure can be controlled by protective clothing.

Worker Exposure

The number of production workers that would be directly exposed to NTA from the manufacturing of laundry and dishwashing detergents in the United States is estimated to be 2,500. The use of NTA would not change the number of workers required to produce detergents at the present market level.

Typical occupational exposure to NTA via airborne detergent dust during detergent formulation has been estimated to be < 4.8 μg/NTA per kilogram per day for an adult male and < 3.6 μg/NTA per kilogram per day for an adult female. This assumes that (a) all the dust is detergent; (b) NTA comprises 25% of the detergent; and (c) 10% of the dust is respirable.

CONSUMER EXPOSURE TO DETERGENTS

Consumer exposure to detergents can result from inhalation of detergent dust, percutaneous absorption from contact with wash water or direct skin contact with the detergent, ingestion of residue on dishes or utensils, and skin contact with residues in clothing.

Number of Consumers Exposed

Laundering Operations--

The number of people in the United States that would be exposed to NTA while doing laundry has been estimated to be 174 million or 81% of the total population if only NTA-containing detergents were available.

Dishwashing Operations--

An estimated 2 million households in the United States use laundry detergents for dishwashing by hand. If each person in the household over 10 years of age washes dishes at sometime, a maximum of 5 million persons would be exposed.

If NTA were used in automatic dishwashing detergents, an estimated 33 million persons would be exposed.

If NTA were used in light duty detergents, an estimated 174 million persons would be exposed since even those households with automatic dishwashers wash dishes (and other kitchen utensils) by hand at sometime.

Residues in Clothing--

Virtually everyone in the United States whose clothes were washed with NTA-containing detergents would be exposed via this route.

Residues on Dinnerware--

An estimated 5.8 million persons would be exposed following hand washing of dishes with an NTA laundry detergent, 40 million persons exposed following dishwashing in an automatic dishwasher, and 214 million persons exposed following hand washing of dishes with a light duty detergent.

Extent of Exposure

Typical consumer exposure to NTA from inhalation of detergent dust has been estimated to be 0.001 μg NTA per kilogram per day (70 kg adult). Exposure to NTA via percutaneous absorption from washing dishes (or laundry, etc.) by hand has been estimated to be 0.13 μg/kg/day (70 kg adult) for a 1/2-hr exposure. The estimated exposure from NTA residues in clothes is 0.018 μg/kg/day (70 kg adult). Exposure by ingestion of NTA from dinnerware has been estimated to be 0.07 μg/kg/day (70 kg adult) for rinsed and towel-dried dishes.

SECTION 3

HUMAN EXPOSURE DURING MANUFACTURE

PRODUCTION TECHNOLOGY FOR TRISODIUM NITRILOTRIACETATE

Trisodium nitrilotriacetate, the sodium salt of NTA, is currently being produced in the United States by Monsanto Company at the Chocolate Bayou Plant near Alvin, Texas, and by the W. R. Grace Company at Nashua, New Hampshire. The combined annual production of the Monsanto and Grace plants is currently at a level of approximately 70 million pounds. Monsanto apparently ships all of its product to Canada for use in detergents. Most of the W. R. Grace Company product is also shipped to Canada, and most of the remainder* is used industrially in the United States. According to information provided by a spokesman for W. R. Grace (Huber, 1978b), Canada currently consumes about 60 million pounds per year of trisodium nitrilotriacetate (i.e., the sum of shipments to Canada from Monsanto and W. R. Grace in the USA). Based on this information, the current use of NTA in the United States can be estimated at 10 million pounds of NTA per year.

The basic process chemistry for the W. R. Grace process according to Huber (1978b) is described by the following chemical reactions.

$$6CH_2O + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O \quad (1)$$

Formaldehyde Ammonia Hexamethylenetetramine (HMT)

$$(CH_2)_6N_4 + 12HCN + 6CH_2O \longrightarrow 4N(CH_2CN)_3 + 6H_2O \quad (2)$$

Hydrogen cyanide Nitrilotriacetonitrile

$$N(CH_2CN)_3 + 3NaOH + 3H_2O \longrightarrow N(CH_2CO_2Na)_3 + 3NH_3 \quad (3)$$

Trisodium nitrilotriacetate

---

* Two divisions of W. R. Grace (in Sweden and in England) purchase "relatively modest" amounts (compared to the total NTA production of W. R. Grace) of trisodium nitrilotriacetate for use in detergents and specialty applications (Amirsakis, 1979).

A representative flow diagram of the W. R. Grace production process for trisodium nitrilotriacetate is presented in Figure 1. The Monsanto plant for trisodium nitrilotriacetate manufacture also uses this W. R. Grace process (with some minor modifications involving principally the type of material conveying equipment) under a licensing agreement (Huber and Amirsakis, 1978).

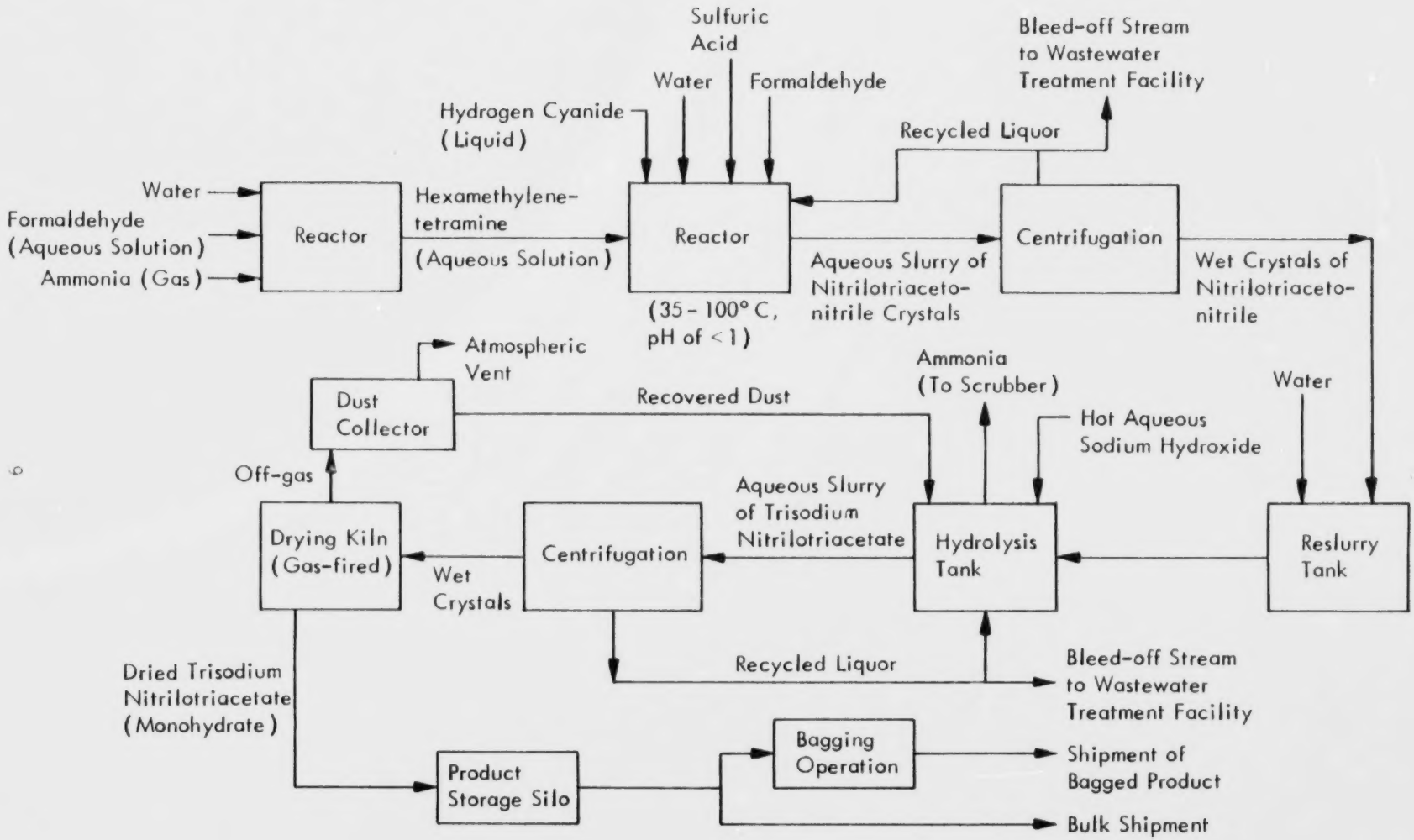
In the first reaction step, formaldehyde in aqueous solution reacts with gaseous ammonia to form a condensation product known as HMT. The yield for this reaction is essentially quantitative. This operation is commonly conducted as a batch operation in a closed system to maintain a supply of HMT.

In a typical operation, an aqueous solution of HMT is added to an aqueous solution containing HCN, formaldehyde, and sufficient acid (sulfuric acid) to maintain the pH of the reaction mixture below 1. The reaction is conducted in the temperature range of 35 to 100 C. The reaction product, consisting of a slurry of nitrilotriacetonitrile crystals, is processed in a centrifuge to separate the crystals from the liquor. The separated liquor is recycled to the reactor.

Wet crystals of nitrilotriacetonitrile discharged by the centrifuge are agitated with water in a reslurry tank to form a slurry. This slurry is added to a hot aqueous solution of caustic soda to hydrolyze the nitrile functions. This reaction results in the formation of a slurry of trisodium nitrilotriacetate crystals and the formation of by-product ammonia which is recovered. This slurry is processed in a centrifuge to separate the crystals from the liquor. The wet crystals are dried in a gas-fired drying kiln. Exhaust gas is passed through a dust collector to an atmospheric vent; recovered dust is recycled to the hydrolysis tank.

Dried trisodium nitrilotriacetate, recovered as the monohydrate, $N(CH_2CO_2Na)_3 \cdot H_2O$, is transferred to a product storage silo. Product is removed from the silo and transferred to a bagging operation or to a bulk shipment station where the material is loaded into hopper bottom railroad cars.

As indicated in Table 2, the typical commercial product purity is greater than 99%. Quantitatively, the most significant impurities are inorganic salts, including sodium hydroxide and sodium carbonate. Also present are small quantities of iminodiacetic acid (IDA). The other impurities such as HCN and trace metals are present at low parts-per-million levels (Winters, 1977). In response to a Midwest Research Institute (MRI) question, a formaldehyde analysis was performed by Monsanto on a plant sample which indicated that the product contained at most 2 ppm formaldehyde (i.e., in the analytical test, any material that releases formaldehyde in acid will give a positive response). Once NTA is formulated into a detergent, it has little tendency to degrade. Under carton/shelf exposure conditions of moisture and air, NTA is completely stable. P&G Canada routinely monitors its NTA-containing detergents (a) as made, (b) in the warehouse, and (c) in the trade; no measurable degradation has been detected.



Source: Huber, 1978 B.

Figure 1. General schematic for commercial production of trisodium nitrilotriacetate.

TABLE 2. IMPURITIES IN TRISODIUM NITRILOTRIACETATE

Impurity	Level	
HCN	4 ± 2 ppm	
NaOH	$0.3 \pm 0.1\%$	
Na_2CO_3	$0.4 \pm 0.1\%$	
Primary and secondary amines	$\sim 0.2\%$	
Iminodiacetic acid (IDA)	$(0.2 \pm 0.05\%)$	
Trace metals (partial)		
K	6 ppm	single batch analyses
Zn	2 ppm	
Cu	1 ppm	
Fe	< 10 ppm	
Pb	1-2 ppm	
Formaldehyde	$\leq$ 2 ppm	

Source: Winters (1977), except formaldehyde from Hopping (1978).

NTA may be oxidized, but it takes a strong oxidizing agent--stronger than present components in detergent products using NTA (Winters, 1978).

There are a number of U.S.-based companies (e.g., Olin Corporation, Geigy Chemical Corporation, Ethyl Corporation) which, although not presently producing NTA domestically, hold patents for its manufacture and could presumably enter the business if market trends warrant such action.

Olin Corporation holds U.S. Patent No. 3,578,709 (May 11, 1971) concerning "Preparation of Alkali Metal Salts of Nitrilotriacetic Acid" (Bishop and Jache, 1971). This method involves heating triethanolamine in the presence of a zinc oxide or cadmium oxide catalyst at 150 to 300°C with a mixture of sodium hydroxide and a minor proportion of potassium hydroxide. The reaction, where M is an alkali metal, is:

$$N(CH_3CH_2OH)_2 + 3\ MOH \longrightarrow N(CH_2COOM)_3 + 6H$$

The Geigy Chemical Corporation holds U.S. Patent No. 3,415,878 (December 10, 1968) concerning "Process for the Production of Alkali Metal Salts of Nitrilo Triacetic Acid" (Gaunt, 1968). The process involves adding an aqueous, mineral-acid-stabilized, equimolar mixture of HCN and formaldehyde to an aqueous solution of an alkali metal hydroxide and ammonia. The reaction is:

$$3HCN + 3CH_2O + NH_3 + 3NaOH \longrightarrow N(CH_2COONa)_3 + 3NH$$

The Ethyl Corporation holds U.S. Patent No. 3,470,245 (September 30, 1969) concerning "Preparation of Nitrilotriacetic Acid" (Jackisch, 1969). The NTA is prepared by the reaction of glycine with carbon monoxide and formaldehyde in the presence of aqueous hydrogen chloride. The chemical reaction is:

$$H_2NCH_2COOH + 2CH_2O + 2CO \xrightarrow[150\text{-}200^\circ C,\ 700\text{-}1{,}000\ atm]{H_2O,\ HCl} N(CH_2COOH)_3$$

ESTIMATED NUMBER OF U.S. PRODUCTION WORKERS FOR NTA

Based on information provided by the manufacturers, the total U.S. plant labor force currently involved in production of NTA is estimated to be 32 workers.

The total number of plant workers required for levels of production larger than 50 million pounds annually can be estimated as follows. Peters and Timmerhaus (1968) have indicated that a "one-fourth factor" can be used to scale up labor requirements from one plant size to a larger plant size. This factor takes into account the fact that larger plant sizes require less than proportional labor forces because of economies of scale.

For a projected NTA production rate of 400 million pounds NTA per year, there would probably be two plants each with production rates of 200 million pounds per year. On this basis, the estimated number of workers required is:

$$2 \times \left(\frac{200,000,000}{50,000,000}\right)^{0.25} \times 20 \text{ workers} = 2.83 \times 20 = 57 \text{ workers}$$

An industry source stated that a production facility with an annual capacity of 300 million pounds would be considered an ideal size based on an optimum size hydrogen cyanide generation plant of 100 million pounds annual capacity. Therefore, MRI chose to limit the annual production capacity of any one plant to no more than 350 million pounds for purposes of this calculation. Thus, the estimated manpower requirement to produce 400 million pounds per year is 57 workers per 24-hr operating day.

If annual production were increased to 1 billion pounds per year, there would probably be three or four plants whose individual total production capacity would average 250 to 350 million pounds per year. Based on the above assumptions, the required labor force per 24-hr operating day is equal to:

$$4 \left(\frac{250,000,000}{50,000,000}\right)^{0.25} \times 20 = 120 \text{ workers, or}$$

$$3 \left(\frac{350,000,000}{50,000,000}\right)^{0.25} \times 20 = 98 \text{ workers.}$$

Thus, the projected labor force for the three production levels is as follows: 70 million pounds (current level) requires 32 workers; 400 million pounds would require 57 workers; and 1 billion pounds would require 98 to 120 workers.

ANALYSIS OF PROBABLE WORKER EXPOSURE TO NTA IN MANUFACTURING OPERATIONS

An analysis of the processing unit operations used in manufacturing NTA was presented in Figure 1.

The entire production process is automated and all workers, except those engaged in product packaging and loading activity, are provided with a remote control room where they spend much of their time in data monitoring and recording activity separated from the process operations. The automatic plant features include process sampling, process material weighing, and transfer and conveying equipment. Air monitors located at various points in the plant area trigger an alarm in the event of any process leaks of toxic material (e.g., HCN).

The first process step involves the reaction of formaldehyde with ammonia to form HMT. The risk of worker exposure in this step appears to be minimal since the reaction is carried out by remote control and the equipment is monitored for gas leaks. The HMT is discharged as an aqueous solution, thus minimizing the possibility of work area contamination with airborne dusts containing process chemicals.

The second reaction step and the subsequent centrifuging step are conducted in a closed system, primarily because of the involvement of highly toxic HCN. Therefore, the risk of worker exposure to reactants, NTA contaminants, or by-products in the operating area for these operations appears to be negligible with the exception of special but controllable exposure hazards which could be created by equipment failure (i.e., breakdown or rupture of equipment resulting in spills or leakage of chemicals to the working area).

The transfer of crystals of nitrilotriacetonitrile from the centrifugation step to the reslurry step is also carried out by remote control, thus restricting worker contact. It appears that the degree of potential exposure in this area would probably be quite low because the crystals are wet and therefore unlikely to create any dust problems.

In the hydrolysis and centrifugation steps, all process operations are carried out in a liquid phase again by remote control. The separated crystals of trisodium nitrilotriacetate are wet and thus the prospects for generation of dust (i.e., skin or inhalation exposure to dusts) in this area appear to be remote. Ammonia formed as by-product during the hydrolysis reaction is recovered.

The wet crystals are dried to produce a powdered product. In the drying step, the off-gas containing fuel combustion products, water vapor, and some dust (sodium salt of NTA) is passed through a dust collector and then vented to the atmosphere. Dust recovered by the dust collector is transferred to the hydrolysis tank for reprocessing.

Dust losses of product are apt to occur to the work atmosphere of the drying kiln, the product packaging area, and the product bulk loading operations. Therefore, the risk of worker exposure via both skin contact and inhalation appears to be greatest for these operations.

In summary, the potential for exposure to NTA during the various steps in the manufacturing process is as follows:

Manufacturing step	Potential for NTA exposure
Formation of HMT	Negligible
Reaction of HMT with HCN	Negligible
Centrifugation and reslurry	Negligible
Hydrolysis and centrifugation	Negligible
Drying	Very large if no precautions employed
Packaging and bulk shipment	Very large if no precautions employed

Proper precautions which can significantly reduce the exposure risk in high exposure operations include:

- Adequate ventilation and dust control equipment.
- Use of proper protective apparel by workers, e.g., gloves, impervious work clothing, and filter masks, or airline breathing masks.

The Monsanto and Grace companies both report that their plants observe these safety precautions.

In summary, since the production of NTA is highly automated and operated by remote control, production workers have a high exposure potential to only the trisodium salt of NTA--the final product--in the bagging and loading operations if protective apparel is not worn. The final product is of at least 99% purity; the contaminants are HCN (4 ppm), sodium hydroxide (0.3%), sodium carbonate (0.4%), primary and secondary amines (0.2%), formaldehyde ($\leq$ 2 ppm), and trace metals (see Table 2, p. 10).

WORKER EXPOSURE DATA

Actual worker exposure data have been compiled at the Monsanto (Chocolate Bayou) facility (Hill et al., 1977). Urine samples were taken for analysis, and air in the breathing zone of each worker was monitored.

Two 24-hr urine samples were collected from each NTA plant worker. Each sample was collected over the 24-hr period approximately in the middle of the workweek. The two samples were taken at approximately 1-week intervals. NTA

was not detected in the urine samples (by GC/MS) at or above the limit of detection 0.5 mg/liter.

Monsanto (Hill et al., 1977) assumed that, since the "metabolism of NTA occurs with excretion of a significant portion (mean value 13%)[a/] of unchanged NTA in urine," urinary levels could be used to measure the exposure to NTA. A 12.3% mean value was reported by Budny and Arnold (1973) who administered 10 mg of NTA orally, in a single dose, to human volunteers; the dose level varied from 0.107 to 0.169 mg/kg. A mean of 12.33 $\pm$ 7.41% of the administered NTA was excreted unchanged in the urine by the subjects. Based upon the 13% excretion level, and assuming that NTA concentrations in the urine were at the minimum detectable level, Monsanto calculated maximum daily intakes which ranged from < 1.69 to < 13.86 mg.

An important question is the validity of using the 13% value for the excretion level; in the Budny and Arnold study, human volunteers received 10 mg orally at one time; however, the air analyses (described later) indicate that the workers were ordinarily exposed by inhalation to 0.1 to 0.5 mg during the entire course of an 8-hr work shift. The lower intake level and the different route of administration could result in substantially different absorption and excretion rates and quantities.[b/] If so, there could be wide variation in the level of exposure which could be detected by urinalysis. For example, if none of the NTA were absorbed or excreted following inhalation, then urinalysis would be incapable of measuring the extent of exposure; if only 1% of the NTA were excreted following inhalation, then exposures of up to 180 mg could not be distinguished from zero exposure.[c/]

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a/ The mean figure stated in the paper by Budny and Arnold was 12.33% in the urine and 76.99% in the feces.

b/ Consultations concerning this question were held with Dr. C. C. Lee, Deputy Director of the Pharmacology and Toxicology Department, Dr. Harry V. Ellis III, Senior Pharmacologist, and Dr. Betty L. Herndon, Associate Pharmacologist, all of MRI. The consensus of opinion was that, in the absence of additional data, one should not assume that 10 mg oral doses and 0.1 mg inhalation doses would result in comparable quantities or rates of NTA excretion. The absorption mechanisms are markedly different and the distribution and excretion patterns could be significantly different.

c/ The upper limit of < 13.86 mg for the daily intake of NTA was calculated by Monsanto (Hill et al., 1977) as follows: urine volume (ℓ) x urine concentration (mg/ℓ) $\div$ 0.13. Substituting 0.01 (1%) for 0.13 yields a daily intake of < 180 mg.

In the air analyses, full period breathing zone monitoring of each worker was performed during the 8-hr shift for which the 24-hr urine sample was collected. "Potential inhalation exposures"[a] ranged from 0.1 to 8.2 mg NTA per shift with a minimum quantitative level of 0.1 mg NTA per day. There were three distinct levels of NTA in the air samples. In the "normal" line area,[b] exposure levels of 0.1 to 0.5 mg NTA per day were usually found. The highest potential exposure was to the hopper-car loader with normal exposure periods of only 30 to 60 min/day. The hopper-car loader had a potential exposure of 8.2 mg NTA per shift. (This potential exposure assumes that the hopper-car loader does not wear a respirator; however, a respirator is required for this operation.) There was one intermediate level of exposure (maximum exposure potential of 5.7 mg/day) which occurred during a plant electrical outage (caused by a rain storm), during which NTA had to be manually removed from carrier belts, and the resulting spills in this area were hosed down the drain.

As shown, calculations based upon the Monsanto data indicate that the worker with the highest potential in inhalation exposure is the hopper-car loader.

Area	Potential exposure[a] (mg NTA/shift)	Time-weighted average concentration[b] (mg NTA/m^3)	Average concentration during shift[c] (mg/NTA/m^3)
Normal line area	< 0.1-0.5[d]	< 0.01-0.05	< 0.01-0.05
Hopper-car loader	8.2	0.82	6.56
During plant outage	5.7 max.	0.57 max.	0.57 max.

a/ From Hill et al. (1977).

b/ MRI calculations. Time-weighted average concentration (mg NTA/m^3) equals potential exposure ÷ 10 m^3 (standard workday tidal volume).

c/ MRI calculations. The actual exposure time for the hopper-car loader was reported to be 30 to 60 min (Hill et al., 1977) and for the purpose of this estimation was presumed to be 1 hr. The other exposure periods were 8 hr (Ward, 1979).

d/ The mean potential exposure was < 0.2 (Plunkert, 1979).

a/ "Potential inhalation exposures" were calculated by Monsanto (Hill et al., 1977) based on the time-weighted average concentration of NTA in the air the the standard workday tidal volume. It was assumed that the worker had no respiratory protection and that no inhaled NTA was exhaled.

b/ Of the three areas in which NTA exposures were measured, the "normal" line area represents all areas other than the area where the hopper-car loader works (Ward, 1979).

The relatively very high concentrations of NTA in the area of the hopper-car loader can also be estimated from other data as follows: Hill et al. (1977) reported that the respirator of the hopper-car loader contained 4.5 mg NTA on one occasion and 7.8 mg NTA on another. If the NTA in the respirator represents the amount collected during a single exposure period (1 hr), the average concentration of NTA in the air can be calculated by assuming that the amount of NTA in the respirator was equal to the amount of NTA in the air inhaled by the worker during the 1-hr exposure period (one-eighth of the standard workday tidal volume, 1.25 m^3). Thus the calculated average NTA concentrations are:

$$\frac{4.5 \text{ mg}}{1.25 \text{ m}^3} = 3.6 \text{ mg/m}^3 \quad \text{and} \quad \frac{7.8 \text{ mg}}{1.25 \text{ m}^3} = 6.2 \text{ mg/m}^3$$

These figures are in general agreement with the calculated level 6.56 mg/m^3.

The following data concerning the exposure of NTA production workers to other products were provided by Monsanto (Metcalf, 1978b).

Ammonia - The American Conference of Governmental Industrial Hygienists (ACGIH) limit is 25 ppm (time-weighted average).

A series of area measurements in the highest exposure potential zones using long-term detector tubes showed ambient concentrations generally below 10 ppm. Considering the limited exposure time of operators in such areas, worker exposures on an 8-hr basis have been calculated to be less than 1.0 ppm time-weighted average. A 10-fold variation in airborne concentrations versus worker time-weighted average exposure is not uncommon in processes having dynamic work patterns.

HCN - The ACGIH limit is 10 ppm (ceiling).

Utilizing long-term detector tubes specific for HCN, the environmental concentrations are for the most part less than the lower detection limit of 0.25 ppm. HCN is handled in completely contained systems where even minor leakage cannot be tolerated. Routine exposure to operators is nil.

Two continuous HCN monitors are located in the NTA unit to alert personnel of possible emergency situations. Both units are set to alarm at 6 ppm.

Formaldehyde - The ACGIH limit is 2 ppm (ceiling).

The exposure information on formaldehyde is more subjective. Formaldehyde, while quite irritating at high concentrations, can be easily recognized at airborne concentrations of 1.0 ppm and detected by experienced personnel at

somewhat lower levels.[a] Monitoring surveys in formaldehyde handling areas using impinger collection followed by colorimetric analysis have substantiated these odor/effect properties.

While little objective monitoring data on formaldehyde exposure in the Monsanto process have been developed to date, the observations and judgment of the plant professionals indicate trace odors of formaldehyde being present in highest potential exposure areas.[b] Area monitoring is scheduled to confirm our assessment of worker exposures being less than the 2.0 ppm ceiling and certainly less than 0.5 ppm on a TWA basis.

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a/ Mr. J. S. Metcalf, Manager, Product Acceptability, Detergents and Phosphates Division, was contacted by Dr. Alfred F. Meiners on June 26, 1979; he stated that the experienced personnel to whom he was referring were not sensitized to formaldehyde, but had simply become skilled in recognizing formaldehyde at concentrations below 1 ppm.

b/ Mr. J. S. Metcalf, Manager, Product Acceptability, Detergents and Phosphates Division, was asked about these areas on February 9, 1979, by Dr. Alfred F. Meiners. Mr. Metcalf said that sampling for formaldehyde was done at a variety of locations throughout the plant. Although he did not remember the exact layout of the plant, he knew that the sampling was done in a number of areas where one would reasonably expect to detect formaldehyde, such as in areas where the reactor was opened and closed.

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SECTION 4

HUMAN EXPOSURE DURING DETERGENT FORMULATION

DESCRIPTION OF DETERGENT FORMULATION PROCESS

The method currently being used for the commercial formulation of granular detergents is primarily a batch process. In the making of powdered detergents, raw ingredients, stored in tanks or bins, are pumped or conveyed through a closed system to reactors and mixers and then blended into a slurry. The slurry is sprayed from the mixer into drying towers to achieve the desired granulation size and moisture content. Additional raw materials can also be added after the drying process. The finished powder is then conveyed to production lines where it is automatically put into cartons and packed for shipping. The industry-wide level of NTA used in powdered detergent currently averages 15% in Canada, where a nationwide limit of 2.2% phosphorus is in effect.

Powdered cleansers are also formulated primarily by a batch process. These products are dry mixes which contain small quantities of detergents. The filling and packing production lines for cleansers can be major sources of dust contamination, particularly in the can filling operation. Liquid laundry detergents are also formulated primarily by a batch process in a closed system. The major steps in this operation include pumping the raw materials from storage tanks into mixers. After mixing, the liquid is bottled and packed by automatic equipment.

AREAS IN EXPOSURE IN DETERGENT PLANTS

The workplace atmosphere can become contaminated with detergent dust containing NTA from abnormal events such as leaks in the product lines and spills caused by a malfunction in equipment; routine and nonroutine equipment cleanup operations can also contribute to worker exposure. Operations which require manual handling of bags of NTA, and the filling and packing production lines can become high dust areas, particularly when powder is spilled as a result of machine jams and product changeovers. In these situations, worker exposure can be controlled by protective clothing.

NUMBER OF WORKERS EXPOSED

The total number of production workers in the entire soap and detergent industry in 1976 was 25,400 (Department of Labor, 1976). The total number of production workers that would be directly exposed to NTA from the manufacture of laundry and dishwashing detergents in the United States is estimated to be less than 2,500. The use of NTA would not change the number of workers required to produce detergents at the present market level.

Procter and Gamble has "somewhat over 1,000 workers" involved in the manufacture of detergents in the United States, and their estimate of current industry-wide exposure to NTA is double that figure, or approximately 2,000 (Winters, 1978a). About 70% (or roughly 700) of the Procter and Gamble workers are involved in the manufacture of granular laundry detergents. Furthermore, only about one-half of these workers enter the dustiest areas of detergent manufacture which are the areas where the detergents are moved, boxed, or packaged (Hopping, 1979).

EXPOSURE LEVELS

Occupational exposure to airborne dust (measured as total dust) during detergent formulation has been measured (Winters, 1978b). The total dust level, as a time-weighted average, was 1.38 µg/liter (1.38 mg/m^3). This figure is an average proportioned by the time spent in the three dustiest areas associated with detergent manufacture. The range of concentrations for these three areas (in micrograms per liter) are: 2.33, 1.11, and 0.67 (Hopping, 1978). It was assumed that a worker spends one-third of his time[a/] in each area. On the basis of these dust levels, the estimated NTA inhalation exposure was calculated (Winters, 1978b) to be:

	Exposure (µg Na_3 NTA/kg/day)	
Person exposed	Typical	Extreme
Adult male (70 kg)	4.8	48.3
Adult female (54 kg)	3.6	35.7

a/ These three areas of higher dust concentrations are those in which the detergent is moved, boxed, or packaged. The average of these three concentration levels (1.38 µg/liter) provides a time-weighted average concentration assuming that a worker spends an equal time in each area. Procter and Gamble believes that this assumption is reasonable; the areas are in close proximity and workers do actually spend approximately one-third of their time in each area (Hopping, 1979).

The calculations were made as follows:

*Breathing rate

Adult male (70 kg), light work $\frac{17.1 \text{ breaths}}{\text{min}} \times 1.673 \frac{\ell}{\text{breath}} = 28.6 \ \ell/\text{min}$

(tidal volume) (Biology Data Book, 1974).

Adult female (54 kg), light work $\frac{19 \text{ breaths}}{\text{min}} \times 0.860 \frac{\ell}{\text{breath}} = 16.3 \ \ell/\text{min}$

(tidal volume) (Biology Data Book, 1974).

*Exposure time - 8 hr/day x 5 days/week = 40 hr/week.

Per day, weekly basis - 40 hr/week x 1/7 day/week = 5.71 hr/day.

The 5.71 hr/day exposure time is on a weekly basis to be comparable to the other estimated exposure.

*Estimated exposure

Adult male $\frac{1.38 \ \mu g/\ell \times 0.25^{a/} \times 28.6 \ \ell/\text{min} \times 60 \text{ min/hr} \times 5.71 \text{ hr/day}}{70 \text{ kg}} =$

48.3 µg/kg/day.

Adult female $\frac{1.38 \ \mu g/\ell \times 0.25^{a/} \times 16.3 \ \ell/\text{min} \times 60 \text{ min/hr} \times 5.71 \text{ hr/day}}{54 \text{ kg}} =$

35.7 µg/kg/day.

These exposure estimates assume that all the measured dust is detergent, that 100% of the dust is respirable, that all of the inhaled dust remains in the body, and that the 7-day breathing rate is that corresponding to light work. These estimates were shown previously as the extreme exposure levels. Industry sources believe that at most no more than 40% of the dust is respirable, and and that in reality < 10% would be respirable. Estimates based on the < 10% figure are shown above as the typical exposure levels.

In our opinion, the Procter and Gamble calculations provide a reasonable estimate of average occupational exposure to NTA in the dustiest areas of detergent manufacture. The calculations were made for a plant actually using NTA for which an average dust level of 1.38 µg/liter was determined. Recent data (Hopping, 1979) indicate that time-weighted average dust levels in these areas in U.S. plants are less than 1 µg/liter. Also, a 25% content of NTA in the

a/ A 25% content of NTA in the detergent is assumed. This would represent maximum concentrations.

detergent is used in the calculations; actual NTA content in Canadian detergent ranges from 0 to 25% with an average of 15% (Brownridge, 1978). Furthermore, in all of the studies, total dust levels were measured, and some of this dust is known to be material other than detergent (Hopping, 1979).

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SECTION 5

CONSUMER EXPOSURE TO DETERGENTS

The total consumer exposure[a/] to detergents includes exposure from:

- Inhalation of detergent dust in home uses.
- Percutaneous absorption from contact with wash water including laundry, dishwashing, and other operations such as mopping floors and general cleaning.
- Percutaneous absorption from skin contact with detergent when measuring detergent, handling the box of detergent, or cleaning a spill of detergent.
- Percutaneous absorption from skin contact with residues in clothes.
- Ingestion of residues left on dishes and utensils.

NUMBER OF CONSUMERS EXPOSED

A summary of the number of consumers potentially exposed to NTA while using selected detergents is presented in Table 3. The underlying assumption of these figures is that all consumers would use NTA-containing products and none would use non-NTA products.

Laundering Operations

The primary exposure from the use of NTA laundry detergents would occur while performing laundering operations. (Subsequent exposures may occur from residues on clothes.) The number of people in the United States that could be exposed to NTA while doing laundry has been estimated to be 176 million (MRI estimate). This figure is based on the estimate that all members of a household over 10 years of age are likely to operate a washing machine at some time (AHAM,

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a/ Another broad segment of the general public would be exposed to NTA in the marketing, transportation, and warehousing of detergents. No attempt was made to estimate the number of persons involved in these operations and no data were available to estimate the extent of their exposure.

TABLE 3. POTENTIAL NUMBER OF CONSUMERS EXPOSED TO NTA VIA DETERGENT USAGE

Product	Use	Route(s) of exposure	Potential No. persons exposed		Remarks
			Total[a]	Most often exposed	
Powdered laundry detergent	Automatic clothes washer	Inhalation	176×10^6	76×10^6[b]	Based on total number of households
	General cleaning and hand laundry	Percutaneous and inhalation	176×10^6	76×10^6[b]	
	Residue on clothes	Percutaneous	212×10^6	212×10^6	Based on total U.S. residential population
	Hand dishwashing	Percutaneous and inhalation	5×10^6	2×10^6[b]	
	Residue on dinnerware[c]	Ingestion	6×10^6	6×10^6	
Powdered dishwashing detergent	Automatic dishwashing	Inhalation	33×10^6	14×10^6[b]	Based on estimated 14×10^6 households with automatic dishwashers
	Residue on dinnerware	Ingestion	40×10^6	40×10^6	
Light duty detergent (liquid)	Hand dishwashing	Percutaneous	171×10^6	60×10^6[b]	Based on number of households using liquid detergent for some type of dinnerware cleaning
	Residue on dinnerware	Ingestion	206×10^6	206×10^6	Total U.S. residential population minus those using powdered laundry detergent
	General cleaning and hand laundry	Percutaneous	176×10^6	76×10^6[b]	

[a] Assumes everyone in household over 10 years of age uses the detergent product at some time.

[b] Industry estimates assuming one person per household uses the detergent product.

[c] Dinnerware includes kitchen utensils.

1978). The Statistical Abstracts compiled by the U.S. Department of Commerce (1978) show the number of households (74.1 million), the average size of the household (2.86 persons), and the percentage of the population over 10 years of age (calculated to be 83%).

However, an industry source estimates that there are only 76 million persons who actually do laundry. This figure is based on the number of households (76 million) and assumes that one person per household does the laundry.[a/] The MRI estimate represents the total number of persons exposed, while the industry estimate represents the number of persons who are most often exposed. (One person per household probably does laundry more often than other household members.)

Dishwashing Operations

In addition to laundry exposure, consumers may be similarly exposed when laundry detergents are used for dishwashing. An industry source estimates that 2 million households in the United States use laundry detergents for dishwashing by hand. Assuming that everyone in the household over 10 years of age washes dishes at sometime, a maximum of 5 million persons would be exposed via this route.

Currently, NTA is not used in any dishwashing detergents in the United States or Canada (Winters, 1978b); however, the potential for the use does exist.

Automatic Dishwashers--

If NTA were used as an automatic dishwashing detergent, the primary exposure would occur while pouring and handling the detergent prior to actual operations. (Subsequent exposure may occur from residues on dishes.) An estimated 33 million persons would be exposed to NTA while using an automatic dishwasher. This figure is based on an estimated 14 million households in the United States with automatic dishwashers, an average of 2.86 persons per household, and an assumption that everyone in the household over 10 years of age will use the dishwasher at some time (MRI estimate). However, an industry source estimates that only one person per household uses the dishwasher; consequently, an estimated 14 million persons would be exposed. The MRI estimate represents the total number of persons exposed, while the industry estimate represents the number of persons who are most often exposed. (One person per household probably uses an automatic dishwasher more often than other household members.)

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a/ Note that the estimates made by industry and by MRI pertaining to the number of households in the United States and the average size of a household are not identical; however, the difference is not significant.

Hand Dishwashing--

If NTA was used in a light duty liquid detergent for dishes, an estimated 171 million persons would be exposed via percutaneous absorption. This estimate is based on the following data:

* 74.1×10^6 total households

* 2.86 persons per household; 83% over 10 years of age

* 14×10^6 households with automatic dishwashers

* 2×10^6 households use laundry detergent for hand dishwashing

MRI assumed that all households, except those using laundry detergent, will wash dinnerware (including kitchen utensils) by hand and that everyone in the household over 10 years of age will be involved. The estimate includes households with automatic dishwashers, since even persons with these machines are likely to wash dishes or kitchen utensils by hand at some time.

An industry source estimates that only 60 million persons would be exposed on a regular basis to NTA from a light duty detergent. This estimate is based on the assumption that only one person per household does dishes, 76 million households, and the same data given earlier for laundry detergent use and automatic dishwashers (2 million and 14 million). It was further assumed that households with automatic dishwashers would not wash any dishes or kitchen utensils by hand.

Currently, most ligh duty detergents are liquid, so that the potential for exposure via inhalation would be minimal. However, the potential for dermal exposure would remain.

Residues in Clothing

Exposure to NTA also occurs from residues in clothes following laundering. Although this exposure is less than when doing laundry, virtually everyone in the United States would be exposed via this route.

Residues on Dinnerware

Exposure to NTA would also occur from residues on dinnerware following dishwashing with an NTA laundry detergent, automatic dishwashing detergent, or light duty detergent if NTA were used in these products. An estimated 6 million persons would be exposed (2.86 persons per household x 2 million) following hand dishwashing with laundry detergent; 40 million persons (2.86 persons per household x 14 million) exposed following dishwashing in an automatic dishwasher; and 206 million persons exposed following hand washing of dishes with a light duty detergent. (Note: Even those households with automatic dishwashers wash dishes and utensils by hand at some time.)

Hand Washing, Mopping, and General Cleaning

Currently, powdered laundry detergents are used for some general cleaning, as well as for washing of clothes. In addition, the use of NTA in cleansers and light duty detergents used for hand washing, mopping, and general cleaning may be considered in the future (industry source, 1978).

Use of detergents containing NTA, intended for general cleaning, would result in the exposure of 176 million persons (MRI estimate). This figure was calculated as before, based on the assumption that everyone in a household over 10 years of age might do hand washing of clothes or general cleaning at some time.

EXTENT OF EXPOSURE

Consumer exposure to NTA if used in detergent products in the United States is most likely to occur during actual use of the product; significantly less exposure is expected from contact with any residues remaining on those items washed in the detergent. A summary of human exposure to NTA through consumer use of detergent products is shown in Table 4.

Exposure by Inhalation

Consumer inhalation exposure to NTA can be expected during use of powdered laundry detergents for washing clothes (and general cleaning) and during use of powdered dishwashing detergent products.

Home Laundry Operations--

The airborne concentrations of detergent expected around a laundry site have been determined by Procter and Gamble Corporation (Hendricks, 1970) and Colgate-Palmolive (Hudson, 1978). From these data, the expected airborne NTA concentrations can be calculated if NTA were used in similar formulations of powdered laundry detergents.

In-home dust collection studies were conducted using a cyclic air sampling device and an electrostatic precipitator during typical consumer use (Hendricks, 1970). The average dust inhalation for an average female was experimentally measured to be 0.27 µg/cup of detergent product used. This figure is based on an adult female inhalation rate of 16.3 liters/min and the double-pour method which is the most common method of dispensing powdered detergent. (The double-pour method involves pouring the product from the carton into a measuring aid and then into the washing machine.) The double-pour method generates more dust than any other method for use of a laundry product in the home (Hendricks, 1970). Consumer usage of laundry detergent was calculated; the average (median) amount used per week is 7.8 cups, and at the upper 95th percentile the figure is 22.5 cups/week. The industry-wide average concentration of NTA in powdered laundry detergents sold in Canada is approximately 15% by weight; the maximum amount that is being used in Canada is 25%.

TABLE 4. POTENTIAL EXPOSURE TO NTA FROM CONSUMER USE OF DETERGENT PRODUCTS

Exposure route	Operation[a]	Subject	Exposure (μg NTA/day)	Remarks
Inhalation	Automatic clothes washer	Male adult	0.140-0.350	
		Female adult	0.050-0.216	
		Child	0.060-0.200	
	Automatic dishwashing	Male adult	0.022-0.140	
		Female adult	0.069-0.054	
		Child	0.010-0.060	
Percutaneous	Hand dishwashing	Adult	8.75-17.5	0.5-0.75 g/ NTA
	Hand laundry	Adult	(same as hand dishwashing)	
	Residue on clothes	Adult	1.28	0.1 μg/cm^3 NTA on fabric
		Child	0.44	
Ingestion	Hand dishwashing	Adult	966.0	No rinse
		Child	968.0	
		Adult	4.90	Rinse, towel dry
		Child	4.80	
	Automatic dishwasher	Adult	4.90-966.0	Same range as for hand dishwashing
		Child	4.80-968.0	

a/ Assumes that only NTA-containing products are in use.

For calculations of consumer exposure, NTA is assumed to be homogeneously distributed throughout all size granules; however, NTA may be preferentially associated with the larger or smaller sized particles. Studies to determine the respirability of detergent dust were not available; consequently, in the estimated exposure to NTA in powdered detergents, exposure to both the respirable and nonrespirable fractions of detergent dust is assumed.

The following is the calculated consumer exposure to NTA via inhalation (Winters, 1978a; MRI calculations) expressed as micrograms of Na_3NTA per kilogram per day.

User	Median	95th Percentile	µg NTA/day
Female adult (54 kg)	0.001	0.004	0.054-0.216
Male adult (70 kg)	0.002	0.005	0.140-0.350
Child (10 kg)	0.006	0.020	0.060-0.200

These data were calculated based on the following formula:

$$\frac{(\text{detergent dust/cup})(\%\ \text{NTA in detergent})(\text{weekly detergent use}) \times (\text{week/day})}{(\text{body weight})}$$

The data used in the calculations are presented below:

- 0.27 µg detergent dust exposure per cup for an adult female, measured in simulated home use, based on an average inhalation rate of 16.3 liters/min (Hendricks, 1970).

- 0.47 µg detergent dust exposure per cup for an adult male, based on simulated home use by Hendricks (1970) and an average inhalation rate of 28.6 liters/min (Biology Data Book, 1974).

- 0.24 µg detergent dust exposure per cup for a 10-year-old child, based on simulated home use by Hendricks (1970) and an average inhalation rate of 14.4 liters/min (Chemical Rubber Company, 1969).

- % of NTA in dust--25% - assumes 25% NTA in detergent with even distribution.

- detergent use--7.8 cups/week - median (Hendricks, 1970); and
  --22.5 cups/week - 95th percentile (Hendricks, 1970).

  Note: Includes other uses such as presoaking, floor washing, etc.

- median (typical) detergent use - the calculations were made as follows:

Adult female $\frac{0.27\ \mu g/cup \times 0.25 \times 7.8\ cups/week \times 1/7\ day/week}{54\ kg} = 0.001$

$\mu g/kg/day$

Adult male $\frac{0.47\ \mu g/cup \times 0.25 \times 7.8\ cups/week \times 1/7\ day/week}{70\ kg} = 0.002$

$\mu g/kg/day$

Child $\frac{0.24\ \mu g/cup \times 0.25 \times 7.8\ cups/week \times 1/7\ day/week}{10\ kg} = 0.006$

$\mu g/kg/day)$

- 95th percentile (extreme) detergent use:

Adult female $\frac{0.27\ \mu g/cup \times 0.25 \times 22.5\ cups/week \times 1/7\ day/week}{54\ kg} =$

$0.004\ \mu g/kg/day$

Adult male $\frac{0.47\ \mu g/cup \times 0.25 \times 22.5\ cups/week \times 1/7\ day/week}{70\ kg} =$

$0.005\ \mu g/kg/day$

Child $\frac{0.24\ \mu g/cup \times 0.25 \times 22.5\ cups/week \times 1/7\ day/week}{10\ kg} = 0.02\ \mu g/kg/day$

Note: These exposure estimates assume that all of the measured detergent dust is inhaled, that all of the detergent dust is respirable, and that all of the inhaled dust remains in the body. This is not expected in actual practice.

The Colgate-Palmolive Company developed a test in 1970 to measure the amount of dust created from the use of several of its products. The test was designed to simulate the use of automatic washing machines. The actual test consisted of four people standing around a bucket 16 in. in diameter and 33 in. above the floor to simulate a washing machine. Each person poured powdered laundry detergent from a 49-oz box into a cup and the cup was emptied into the bucket. This was repeated until the boxes were empty. An air sampler was situated in an area which would be occupied by a fifth person around the bucket. The sampling was performed during the pouring of the detergents and for various time intervals after the pouring was complete (Hudson, 1978). The results of this study are presented in Table 5.

TABLE 5. DUST LEVELS FROM POWDERED DETERGENTS

Product No.	Total pouring time for 49 oz (min)	Total sampling time (min)	Total amount of dust collected ($\mu g/m^3$ of air)	Calculated amount of dust created by 1-1/4 cup over the sampling period ($\mu g/m^3$)
1	2	50	1,400	93
2	2	100	2,000	133
3	2	124	300	20
4	2	126	300	20
5	2	200	800	53

Source: Hudson (1978).

Ninety-five percent of detergent dust settles in 100 sec, virtually all detergent dust settles within 2 min (Hendricks, 1970). This information is based on a study using a laser dust detection device developed for this study.

Assuming the breathing rates used in the Procter and Gamble study and an average breathing time of 2 min, the extent of exposure to the levels generated in the Colgate tests were estimated (Table 6). These values, which utilize dust concentrations determined by the Colgate-Palmolive Company, are within the range of exposures calculated in the Procter and Gamble study.

TABLE 6. INHALATION EXPOSURE TO NTA-CONTAINING POWDERED DETERGENT

Detergent product No.	For adult female[a/] (μg/kg)	For adult male[a/] (μg/kg)
1	0.014	0.019
2	0.020	0.027
3	0.003	0.004
4	0.003	0.004
5	0.008	0.011

Source: MRI calculations.

a/ Calculated as follows: breathing rate (16.3 liters/min, female; 28.6 liters/min, male) x exposure time (2 min) x dust concentration (μg/liter (Table 5) x 1 m^3/1,000 liters) x maximum NTA content of detergent (0.25 ÷ average body weight (54 kg, female; 70 kg male) = estimate.

Automatic Dishwashing Operations--

The potential inhalation exposure to NTA associated with automatic dishwasher detergent use has not been studied. However, inhalation exposure from its use in an automatic dishwasher detergent is assumed to be similar to exposure estimated for laundry detergent (MRI estimate). Two differences should be noted: (a) the dishwashing detergent is poured directly from the box to the dishwasher and is not double-poured as with laundry operations; and (b) the average quantity of dishwashing detergent employed per load [2.5 tablespoons (0.16 cup) versus 1 cup] is considerably smaller. On a per cup basis (assuming a daily consumer use of 1 cup/day maximum; MRI estimate), the detergent dust exposure would be 0.27 μg for an adult female, 0.47 μg for an adult male, and 0.25 μg for a child, resulting in potential dust exposures of 0.001, 0.002, and 0.006 μg/kg/day, respectively. For an average per load usage of 0.16 cup, these maximum values should be reduced by a factor of about 6.25. These data were based on the following formula:

$$\frac{(\text{detergent dust exposure/cup})(\%\ \text{NTA in detergent})(1\ \text{cup/day})}{(\text{body weight})}$$

The maximum percentage of NTA that is currently being employed in Canada for granular laundry detergents is 25%. That percentage has been assumed for these calculations.

Exposure by Percutaneous Absorption

Percutaneous exposure can result from washing dishes, hand laundry, and general cleaning with a detergent containing NTA, contact during laundry machine operation and contact resulting from wearing clothes which have been washed in a detergent containing NTA.

Hand Laundry and Dishwashing--

The following calculation summarizes exposure to NTA if it were added to laundry detergent or light duty detergent (liquid or powdered) and used to wash dishes or laundry by hand (Winters, 1978a).

- calculation

$$\frac{(\text{24 hr absorption}) \times (\text{skin area}) \times (\text{exposure time})}{(\text{body weight})}$$

- data

24-hr absorption 0.25 $\mu g/cm^2$/day--highest measured for animal skin exposed for 24 hr to a solution of NTA and linear alkylbenzene sulfonate (LAS), each present 0.2% (wt/vol).[a/]

Note: A typical concentration for doing dishes or laundry by hand would be 0.2 to 0.3% (wt/vol) detergent and the typical NTA concentration in the wash water for doing dishes (and laundry) by hand is 0.050% (0.5 g/liter) to 0.075% (0.75 g/liter), assuming an NTA level of 25% in the product (Winters, 1978c). This concentration is about two times the concentration used in automatic laundry machines (Hopping, 1978a; Winters, 1978c).

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a/ A study was conducted in 1974 (Hopping, 1979) to determine the skin absorption potential of NTA. The experiment consisted of a single application of carbon-14 labeled NTA and LAS (each present at 0.2%) to the shaved skin of two rats. The animals were restrained for 72 hr and the urine and feces collected. The results showed a maximum 24-hr absorption of 0.25 $\mu g/cm^2$ for NTA.

Rat skin does not provide a simulation of human skin and is not commonly used for this purpose. Shaved rat skin generally permits greater penetration of chemicals than occurs through human skin so that the absorption rate is probably greater than that which would occur through human skin under normal conditions. Additional tests would need to be performed on other animal skin models before a more precise approximation of human skin absorption can be assumed (Herndon, 1979). However, the calculated exposure given here probably represent an upper limit for the above reasons.

- exposure time--1 hr/day--95th percentile, is 3.85 washes/day at about 15 min/wash; 0.5 hr/day--median, is about 2 washes/day at about 15 min/wash (Hendricks, 1970).

- exposure area--1,680 cm^2 hand and forearm area for 70 kg adult (Winters, 1978a).

1 hr/day exposure $\frac{0.25\ \mu g/cm^2/day \times 1{,}680\ cm^2 \times 1\ hr/24\ hr}{70\ kg} = 0.25\ \mu g/kg/day$

0.5 hr/day exposure $\frac{0.25\ \mu g/cm^2/day \times 1{,}680\ cm^2 \times 0.5\ hr/24\ hr}{70\ kg} = 0.13$ $\mu g/kg/day$

Note: Absorption flux used was measured at an NTA concentration higher than that which would be found in actual practice. The calculations also assume that absorption for human skin is the same as that for the animal skin.

No data have been found concerning the exposure which could occur if concentrated solutions of detergent containing NTA came in contact with the skin. Similarly, skin absorption from contact with NTA products (laundry or dishwashing) in the powdered form has not been studied. The number of people exposed in this manner would be very large (all persons who handle boxes of detergents), but the contact time would probably be short compared to contact with dishwater. (Most people would rinse their hands shortly after contact with powdered detergent.) The percutaneous data provided by Procter and Gamble (Winters, 1978a) indicate that a 70 kg adult would be exposed to only 0.13 to 0.25 $\mu g/kg$ of NTA per day resulting from exposure to dishwater containing a concentration of 0.2% (wt/vol) (2.0 g/liter) NTA. However, exposure of the dishwasher or launderer to detergent adhering to the container (or other sources of contact with the powder, such as spills) possibly results in a situation where a fairly highly concentrated solution of the detergent would be in contact with the skin (of the hands, particularly). No data are available to predict the percutaneous absorption rate of higher concentrations of NTA.

Laundry Machine Operations--

The NTA concentration expected in laundry machine washwater is 0.36 g/liter (0.036% wt/vol). This figure was calculated from the following data (Winters, 1978c; Hopping, 1978a).

- 1.25 cups detergent

- 77 g of detergent per cup

- 25% NTA

- 17.5 gal. wash solution volume

Contact with laundry machine washwater does not occur frequently, and when contact occurs it is usually of short duration. (Most people would rinse their hands following such contact.) Because of the infrequent and short duration contact time, no exposure level calculations were performed.

Residue in Clothes--

The extent of consumer exposure to NTA in clothes has been estimated by Procter and Gamble (Winters, 1978a; Hopping, 1978b; Hopping, 1979) using the following method:

$$\frac{(\text{conc. on fabric}) \times (\text{skin area exposed to fabric}) \times (\text{absorption efficiency})}{\text{body weight}}$$

The data employed were:

- concentration on fabric of 0.01 $\mu g/cm^2$; measured value for fabric laundered in NTA detergent.
- skin area exposed, assume complete coverage 24 hr/day: adult, 1.6 x 10^4 cm^2 (70 kg); child, 5.5 x 10^3 cm^2 (20 kg)
- absorption efficiency, 0.8%--highest measured for animal skin exposed *in vitro* for 24 hr to a solution of NTA and LAS, each present at 0.2% (wt/vol). The average NTA concentration in automatic laundry machine washwater is 0.036% (wt/vol), assuming 25% NTA in the detergent.

  Note: A typical product use would be about 0.12% (wt/vol) of powdered laundry detergent [i.e., 0.03% NTA (wt/vol)].

The estimated exposures are:

$$\text{Adult } \frac{0.01\ \mu g/cm^2 \times 1.6 \times 10^4\ cm^2/day \times 0.008}{70\ kg} = 0.018\ \mu g/kg/day$$

$$\text{Child } \frac{0.01\ \mu g/cm^2 \times 5.5 \times 10^3\ cm^2/day \times 0.008}{10\ kg} = 0.044\ \mu g/kg/day$$

Note: Not all body skin area is covered with clothes.

Exposure by Ingestion

This section describes potential exposure to NTA via ingestion if NTA were formulated into dishwashing detergents. To the best of our knowledge, NTA is not currently used in the United States or Canadian dishwashing detergents in either automatic dishwashing formulations or in light duty detergents (those intended for hand dishwashing).

Residues Resulting From Hand Washing of Dishes--

One percent of households doing dishes by hand do not rinse their dishes (industry source, 1978). The following calculations summarize NTA exposure from residue on dinnerware resulting from washing dishes by hand and applies to both rinsed and nonrinsed dishes (Winters, 1978a). In these calculations, it has been assumed that all households (76×10^6) will, at sometime, wash dishes or kitchen utensils by hand.

- calculation method

$$\frac{\text{(deposition on dinnerware)} \times \text{(area of dinnerware use)} \times \text{(\% of area in contact with food)}}{\text{(body weight)}}$$

- data

  Deposition on dinnerware 0.45 $\mu g/cm^2$--measured by chemical analysis for 25% NTA laundry product used at 0.2% (wt/vol) for dishwashing (rinsing and towel drying substantially reduces this amount); daily dinnerware area 4,300 cm^2/person; percentage of dinnerware area in contact with food 50% (or 2,150 cm^2).

- estimated exposure

  No rinse/drain dry--Adult $\frac{0.45\ \mu g/cm^2 \times 4{,}300\ cm^2 \times 0.50}{70\ kg} = 13.8\ \mu g/kg/day$

  --Child $\frac{0.45\ \mu g/cm^2 \times 4{,}300\ cm^2 \times 0.50}{10\ kg} = 96.8\ \mu g/kg/day$

  Rinse/towel dry--

  Adult $\frac{0.45\ \mu g/cm^2 \times 4{,}300\ cm^2 \times 0.50 \times 0.05 \times 0.10}{70\ kg} = 0.07\ \mu g/kg/day$

  Child $\frac{0.45\ \mu g/cm^2 \times 4{,}300\ cm^2 \times 0.50 \times 0.05 \times 0.10}{10\ kg} = 0.48\ \mu g/kg/day$

  Note: Rinsing dilutes concentration of adhering solution by 1/20; hence, 0.05 in equation. Towel drying removes 90% of adhering solution; hence, 0.1 in equation.

- hand dishwashers that do not rinse: One percent of the 74×10^6 households which do dishes at sometime by hand do not rinse; this equals 74×10^4 households doing dishes and not rinsing ($0.01 \times 74 \times 10^6$). Total persons affected, 201×10^6 (74×10^4 households x 2.83 persons/household).

- hand dishwashers who do rinse, followed by towel or drain dry: 99% of hand dishwashers; 75 x 10^6 households (0.99 x 76 x 10^6) do dishes by hand, rinse, and towel dry; total persons affected, 212 x 10^6 (75 x 10^6 households x 2.83 persons/household).

Residue Resulting From Use of an Automatic Dishwasher--

The concentration of NTA in the wash water of an automatic dishwasher would be the same concentrations as estimated for hand washing of dishes (MRI estimate) with an NTA laundry product, i.e., 0.05% (0.5 g/liter) to 0.075% (0.75 g/liter). This is based on a 0.2 to 0.3% (wt/vol) concentration of detergent in water and an assumed level of 25% NTA in the automatic dishwasher detergent.

The estimated exposure to NTA from residue on dinnerware following washing in an automatic dishwasher for an adult is estimated to be between 13.8 µg/kg/day (the estimated exposure when hand washed dishes are not rinsed) and 0.07 µg/kg/day (exposure when hand washed dishes are rinsed and towel dried) (MRI estimate). For a child the upper and lower limits would be 96.8 and 0.48 µg/kg/day. These exposure estimates are most likely high because the hot water rinses of an automatic dishwasher cycle could lead to less residue on dinnerware than hand wash and rinse.

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